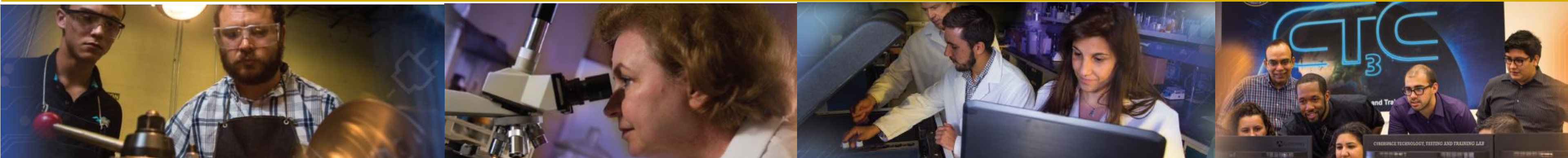
FIU PROJECT 2: YELENA KATSENOVICH

ENVIRONMENTAL REMEDIATION SCIENCE & TECHNOLOGY

Florida International University



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Project Tasks and Scope

Task 1: Remediation Research and Technical Support for the Hanford Site

- Laboratory-scale experiments to study impacts of potential *in situ* remediation techniques on the subsurface at Hanford.
- Investigate geophysical techniques for tracking remediation progress

Task 2: Remediation Research and Technical Support for Savannah River Site

- Laboratory-scale experiments to study impacts of potential *in situ* remediation techniques on the subsurface at SRS.

Task 3: Surface Water Modeling of Tims Branch

- Development of a hydrological model of Tims Branch watershed at SRS.

Task 5: Research and Technical Support for WIPP

- Laboratory-scale experiments to study the fate of actinides and lanthanides at the WIPP site.

Task 1: Remediation Research and Technical Support for the Hanford Site

Site Needs:

DOE-EM has a critical need to understand the biogeochemical processes influencing the behavior of contaminants (U(VI), Tc-99) in Hanford Site's deep vadose zone that can impact groundwater. Research to address environmental risks and remediation challenges involving Tc-99 is a high-priority activity for the DOE-EM complex. Manipulation of pH via ammonia gas is a potential remediation technology that can lead to incorporation of U(VI) into the sediments. Improving geophysical response for contaminant behavior and remediation performance can assist environmental remediation.

Year 7 Objectives:

- Identify controlling mechanisms that lead to immobilization of U via NH_3(g) injection.
- Evaluate if soil bacteria play a role in the release of U in the aqueous phase by autunite dissolution, secondary mineral formation and potentially U(VI) bio-reduction.
- Investigate spectral induced polarization (SIP) signatures of microbial activity to test if microbial actions are detectible via SIP and analyze the resulting SIP data.
- Investigate if Tc(IV)-carbonate complexes represent an important mechanism for technetium migration in anaerobic environments.

Present (Year 7) Subtasks:

1. Compare removal of U following base treatment with NaOH, NH_4OH and NH_3 gas in batch samples in the presence of Hanford relevant minerals
2. Investigate microbial-meta-autunite interactions focusing on autunite dissolution in the presence of bicarbonate
3. Measure electrical geophysical responses to microbial activity in saturated environments via column experiments
4. Determine the partitioning of Tc-99 between aqueous phase and Hanford soil in the presence of bicarbonates under reducing conditions

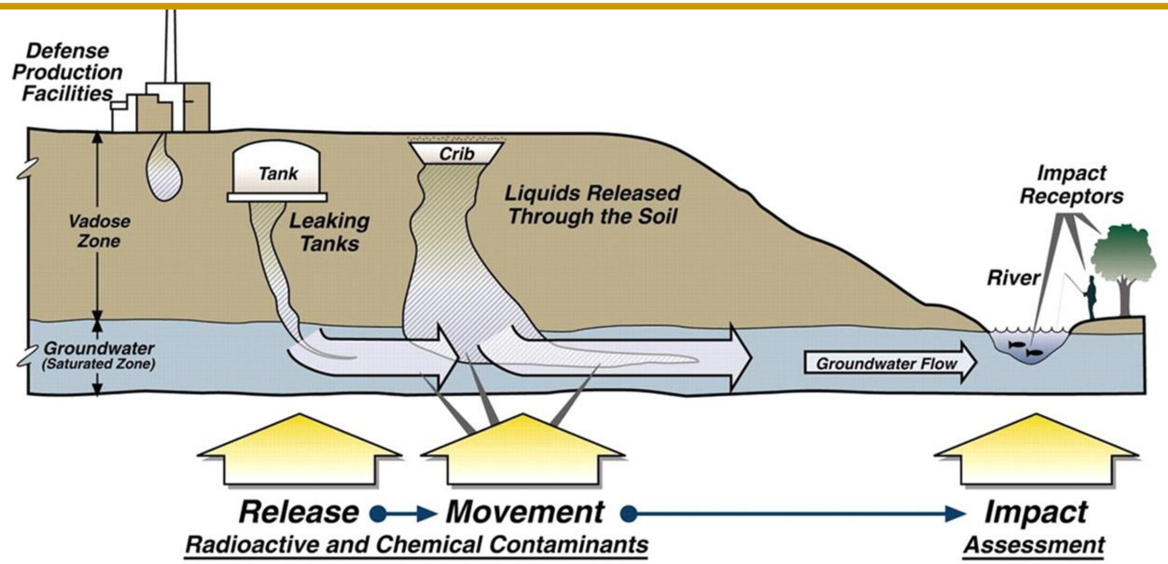
Remediation Research for Hanford

Ammonia Gas Injection

Ammonia gas as a potential technology for U remediation

- No additional liquid added to vadose zone
- Uranium becomes incorporated into the sediments

<u>Goal:</u> Explain the basic scientific mechanisms that lead to immobilization of U via NH_3(g) injection



Remediation Research for Hanford

Ammonia Gas Injection

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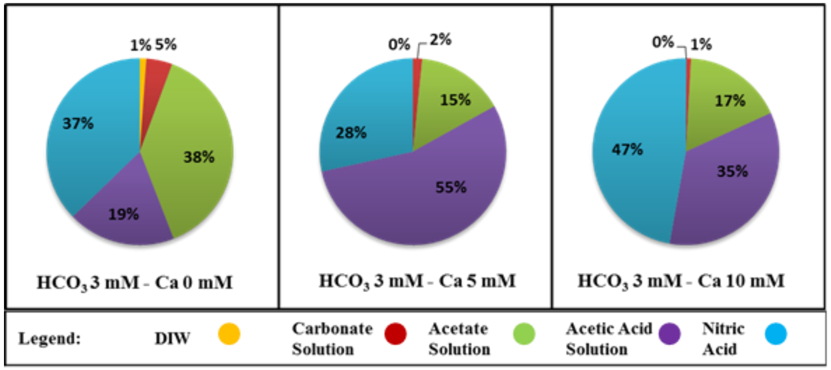
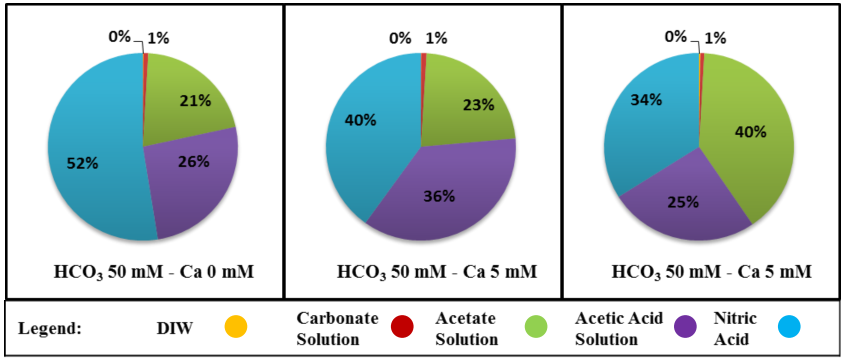
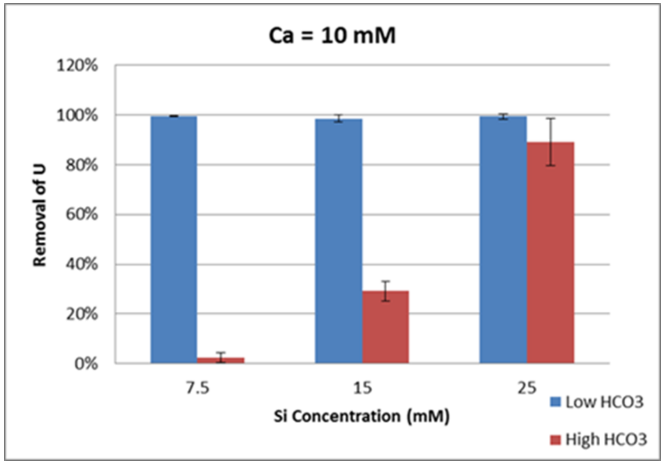
Uranium Extraction Distribution for low HCO_3 samples



Uranium Extraction Distribution for high HCO_3 samples





Research Highlights:

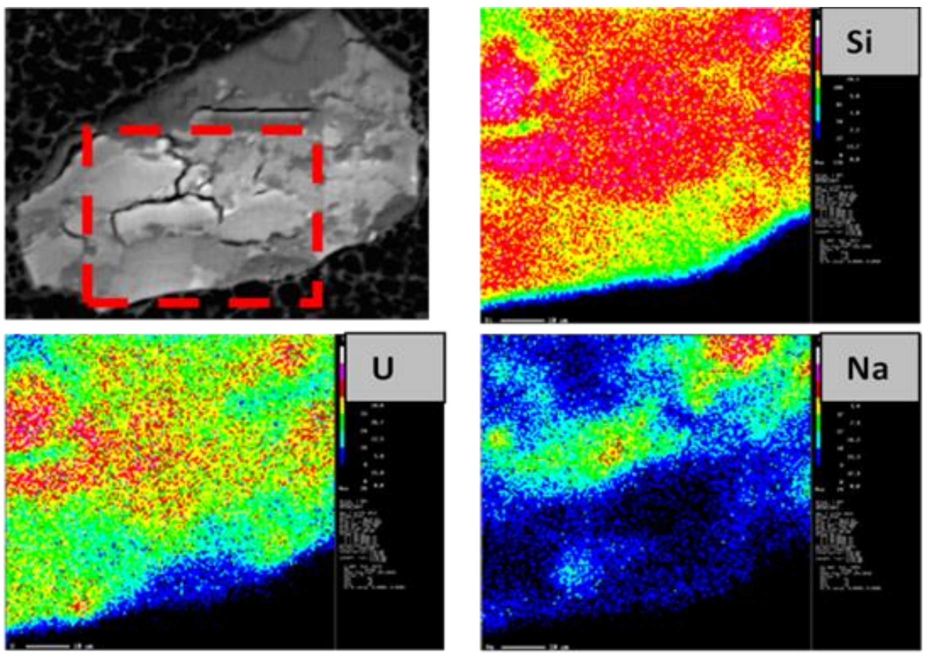
- Most U is in the uranyl silicates phases (based on sequential extractions and EMPA).
- Low concentration of Si increases U removal at lower pH (pH 11 versus 12), i.e. less NH3 gas addition required
- More Si is necessary for removal at higher HCO_3^- concentrations due to uranyl carbonate formation

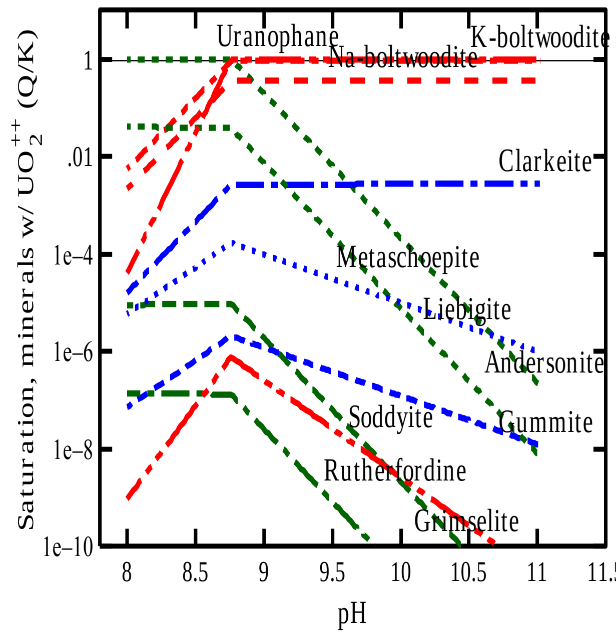
Remediation Research for Hanford

Ammonia Gas Injection

Research Highlights:

- The correlation between Si and U in microscopy suggests uranyl-silicate phases.
- Results are also consistent with sequential extractions and predictive speciation modeling (i.e. boltwoodites).





EPMA micrograph and corresponding elemental maps provided visual comparisons of the elemental associations present in the polished surfaces of uranium-bearing samples through high spatial resolution elemental analysis.

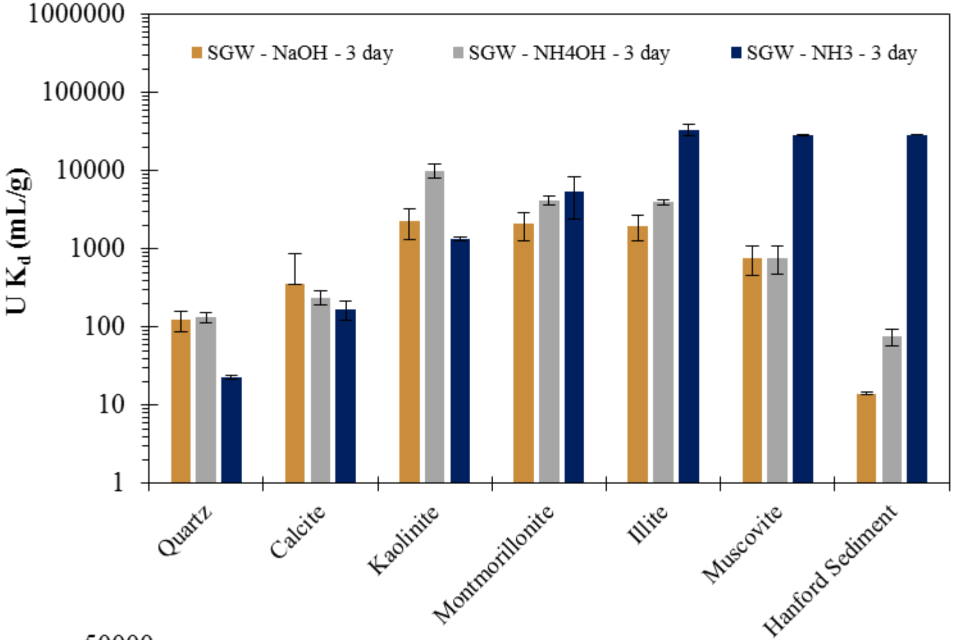
Remediation Research for Hanford

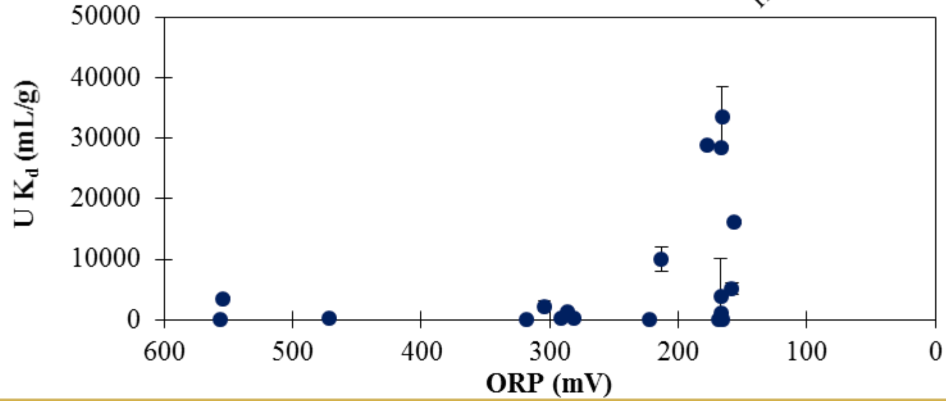
Ammonia Gas Injection

Research Highlights:

- Investigated U partitioning and mineral dissolution following base treatments (NaOH, NH_4OH, and NH_3 gas).
- Demonstrated that greater removal of U occurs in the presence of illite, muscovite and Hanford sediments for ammonia gas treatment than other minerals.
- Showed significant changes in redox conditions with treatments and potential for U reduction.

Condition	ORP (mV)
Initial	527±48
NaOH	296±15
NH_4OH	187±28
NH_3	150±15





Remediation Research for Hanford

Ammonia Gas Injection

FIU Applied Research Center

Future Aims for FY8:

To understand impacts of base treatment on *muscovite*, *illite*, and *Hanford sediments,**

- Physical and mineralogical changes due to dissolution and precipitation
- Speciation of U in the solid phase due to sorption and co-precipitation
- Stability of solid U phases

To be accomplished via

- Characterization of mineralogy via XRD and TEM, Surface area and morphology via BET and SEM, Analysis of U per EMPA, HRTEM, and SEM-EDS (EMSL proposal submitted)
- Predictive Geochemist WorkBench® Speciation modeling

Accomplishments:

- Publication in *Journal of Environmental Radioactivity* and Waste Management Conference Proceedings
- Presentations at ACS Fall 2016, WM2017, ACS Spring 2017, Miami March for Science, and eMerge Conference
- Di Pietro received 2nd place in the WM student poster competition

*Due to similar removal during ammonia gas treatment, we hypothesize that these may be the controlling minerals or at least exhibit similar removal processes

Remediation Research for Hanford

New Task 1.5. Stability of Contaminants in Carbonate Precipitates

FIU Applied Research Center

Site Needs:

- Currently, the DOE has no approved treatment technologies for subsurface iodine plumes. However, historical ^{129}I releases have resulted in massive, dilute plumes in the subsurface of the Central Plateau at the Hanford Site. Studies conducted previously confirmed that iodine removal from the aqueous phase can occur through incorporation into calcium carbonate. PNNL results indicate an increased removal of co-contaminants, such as chromate, during calcite precipitation (PNNL-24709).

Objectives

- Synthesize calcium carbonate minerals in the presence of co-contaminants (including U, I, Cr) in the presence of silica.
- Investigate the stability of contaminants substituted in calcium carbonate materials in the presence of silica at different pH conditions pertaining to the Hanford Site.

Remediation Research for Hanford

Microbial Dissolution of Uranyl Phosphate

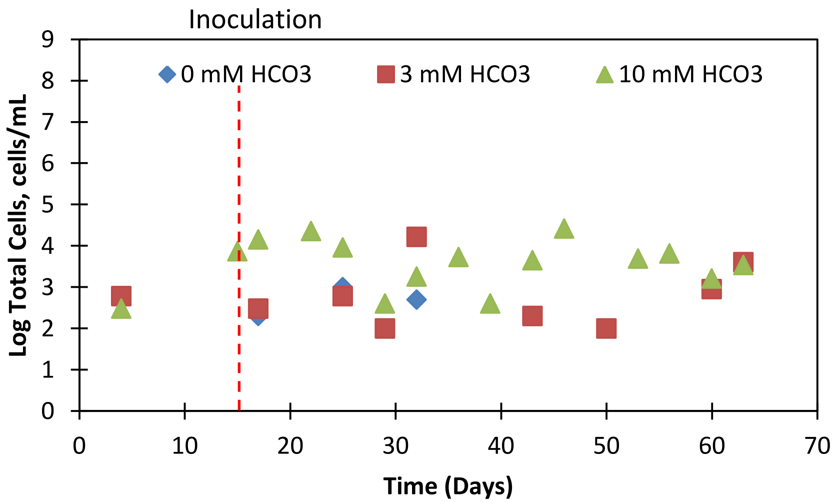
FIU Applied Research Center

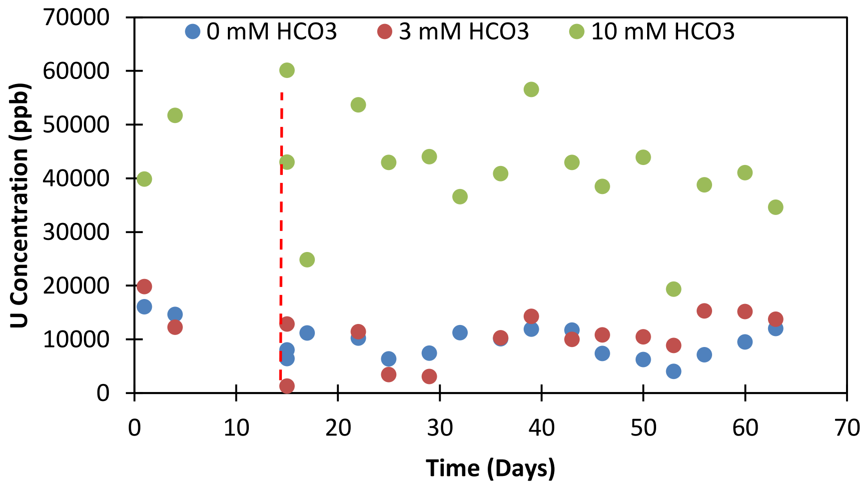
Site Needs:

Research considering the impact of microbes on contaminant mobility is important to determine the long-term stability of precipitated uranium after sequestration efforts via polyphosphate injections.

Experiments with synthetic Na-autunite under trace O_2 conditions using duplicate sacrificial vials:

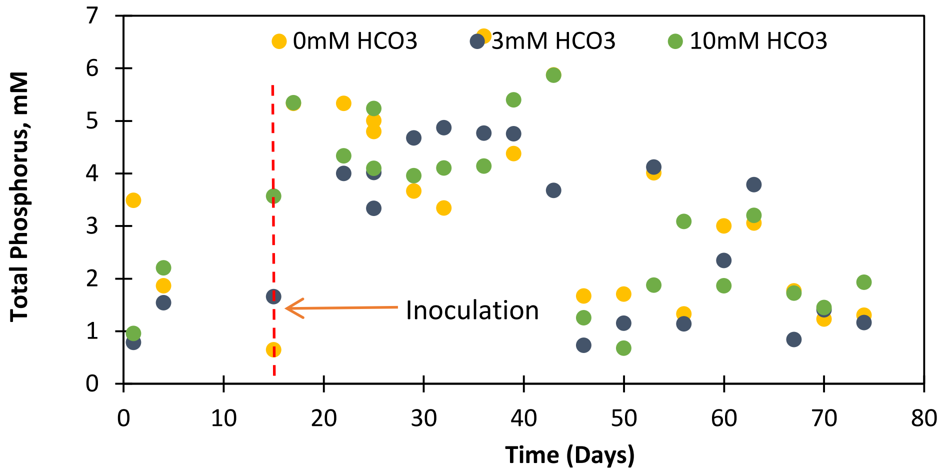
- No reduction of U(VI) to U(IV) was observed.
- Cell density was the same under each concentration of bicarbonate.
- For HCO_3-free samples and 3mM HCO_3, U(VI) concentrations were at similar levels.
- 10 mM HCO_3 samples slightly increased at the beginning but then stabilized close to original concentration before inoculation.

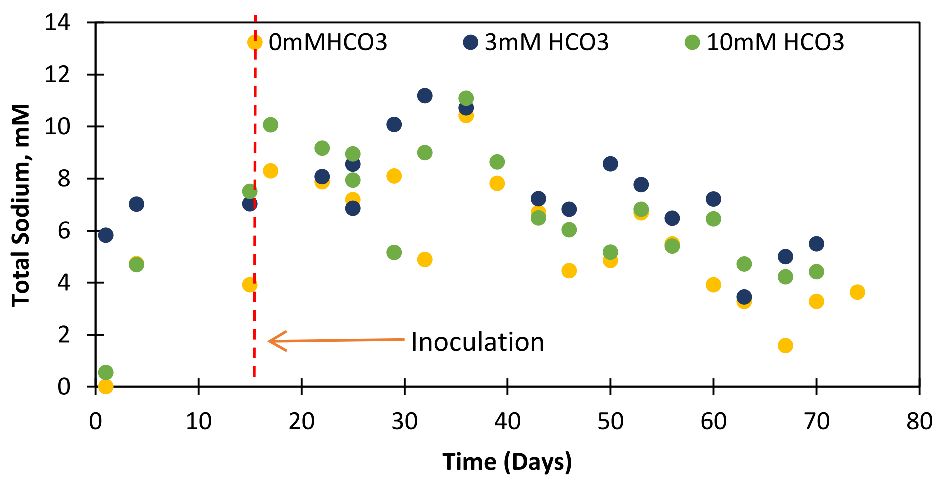




Remediation Research for Hanford

Microbial Dissolution of Uranyl Phosphate





Research Highlights:

- There is no significant difference between Na and P concentrations for bicarbonate concentrations tested.
- The biodissolution influences incongruent reactions to release Na and P from the mineral structure.
- The decrease in Na and P suggests the formation of secondary phases (GWB speciation modeling).
- Currently running biodissolution experiment for consortia culture.

Proposed Scope for FY8:

- Finalize microbial consortia biodissolution experiments.
- Compare results with columns inoculated with microbial consortia (geophysics task).

Remediation Research for Hanford

Geophysical Response of Microbes

FIU Applied Research Center

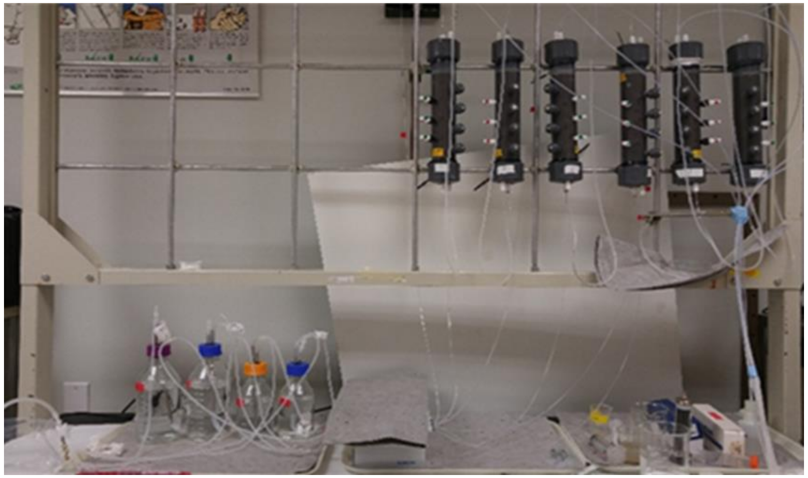
Site Needs:

Research on environmental remediation requires knowledge deep vadose zone contaminant distributions and may be accomplished using geophysical techniques. FIU is conducting column experiments to test the feasibility of corresponding electrical geophysical response to measure microbial activity spurred by ongoing remediation efforts for uranium.

Spring 2016
- Student internship at PNNL
- Exchange of knowledge of geophysical techniques

2016 - 2017
- Master's thesis based on techniques learned at PNNL
- FIU experiments on saturated columns

2017-2018 Future
- Unsaturated column experiments;
- Identify future knowledge gaps using geophysical monitoring



Geophysical columns set up at FIU
- Soil layer mixed with Ca-Uranium-phosphate (autunite)
- Magnetite in soil composition

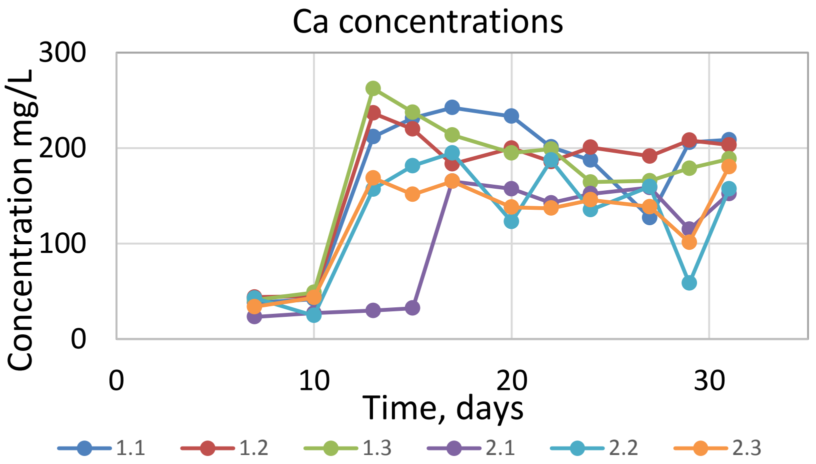
Remediation Research for Hanford

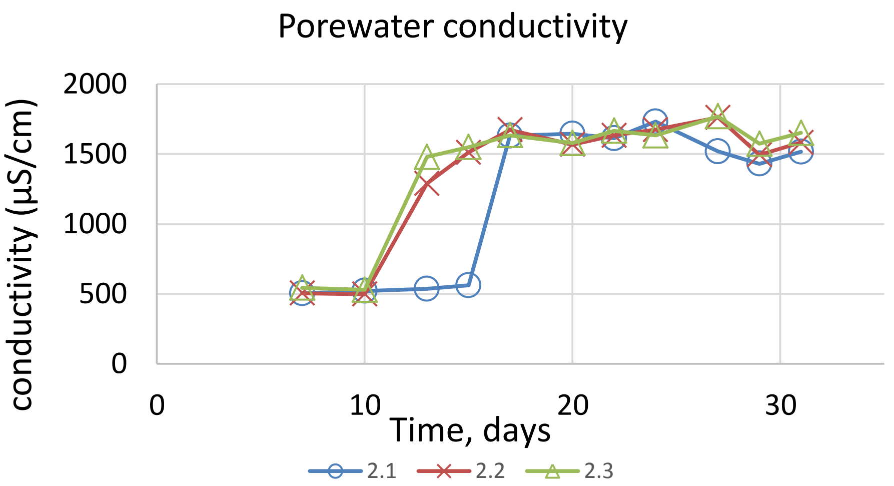
Geophysical Response of Microbes

Applied Research Center

Accomplishments:

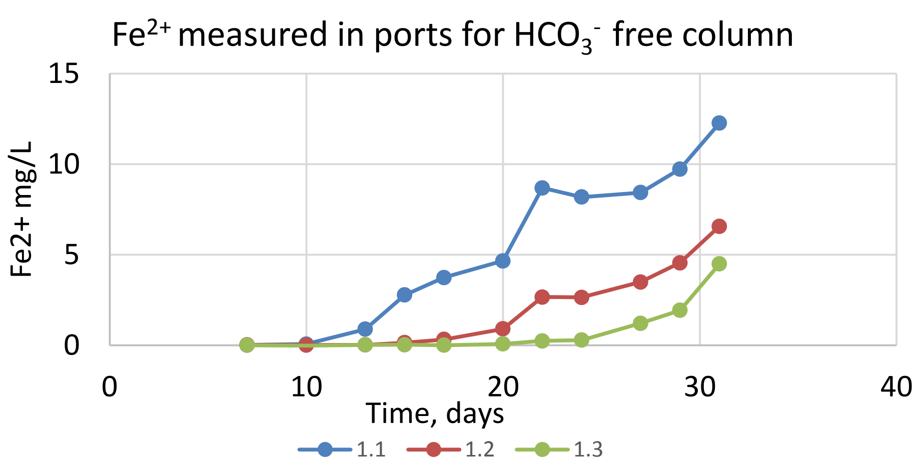
- Performed column experiments measuring spectral induced polarization (SIP) signatures using PNNL provided microbial consortia enriched from Hanford Site sediment.
- Analyzed changes in pore water quality for conductivity, pH, ORP, Mg, Fe^{2+}, total Fe, Ca, P, U(VI).
- Completed a technical report on January 30, 2017.

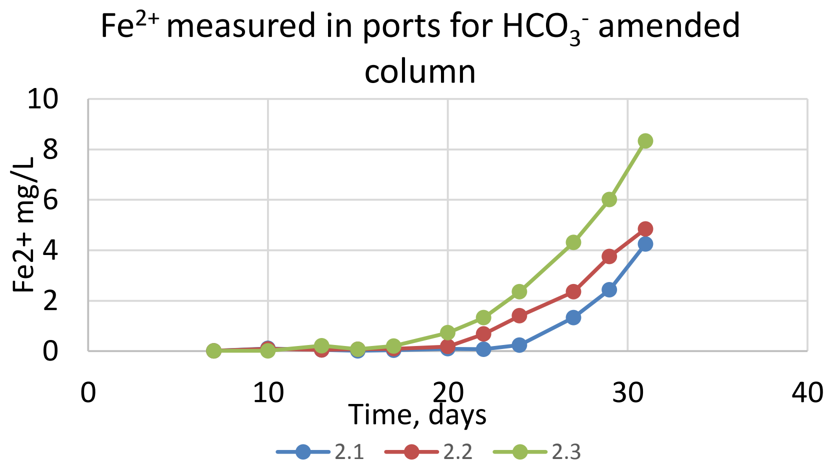


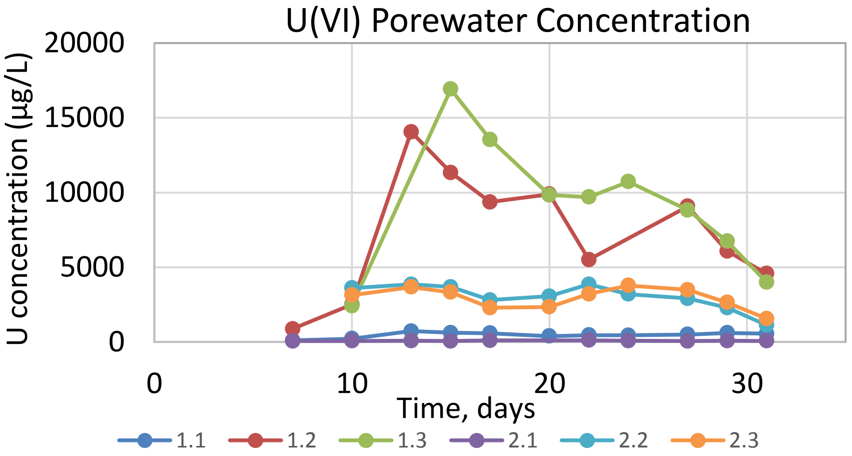


Remediation Research for Hanford

Geophysical Response of Microbes - Accomplishments





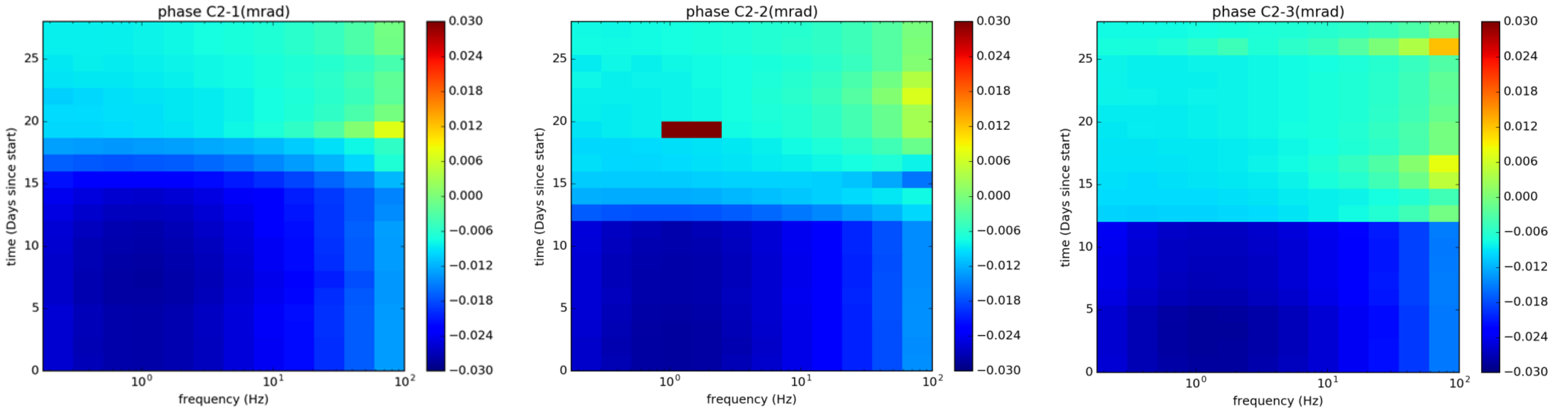


Research Highlights:

- Conductivity measurements follow the same trend as of Ca/Mg concentrations.
- Decrease in U(VI) concentration coincided with an increase in Fe^{2+}
- Preliminary speciation modeling results suggested U(VI) reduction to U(IV).
- Soil samples collected from ports are ready for SEM/EDS analysis.

Remediation Research for Hanford

Geophysical Response of Microbes



Research Highlights, cont'd

- SIP cannot distinguish the bacterial films; however, it detects changes indicative of bacterial activities in pore water composition.
- A clear change in the phase and conductivity.
- Additions of glucose alone was not responsible for changes because it has no charge.
- Phase measures a combination of effects from the drastic changes from bacterial activities on the surrounding environment.

Proposed Scope for FY 8

- Conduct unsaturated column experiments for comparison to FY7.
- Each column will be filled with Hanford sediment and a layer of autunite as previously.
- Soil moisture will be on the level of 7-10% prepared with solutions used for the saturated column experiments.

Remediation Research for Hanford

Investigate the fate of Tc under conditions relevant to the Hanford Site

FIU Applied Research Center

Site needs

- DOE-EM has a critical need to address challenges associated with Tc-99 remediation of the contaminant plumes in deep vadose zones. It requires understanding of Tc chemistry in oxic-anoxic conditions in the presence of bicarbonates, a major ion in Hanford's pore water, which will allow the design of more effective remedial strategies.
- Understand Tc oxidation state and partitioning between soil and aqueous phase under reducing conditions and identify the role of bicarbonate on Tc environmental mobility (Tc4+- carbonate complexes).
- Determine the role of reactive mineral phases, such as magnetite and ilmenite, in the sequestration/immobilization of Tc and quantify sorption parameters.

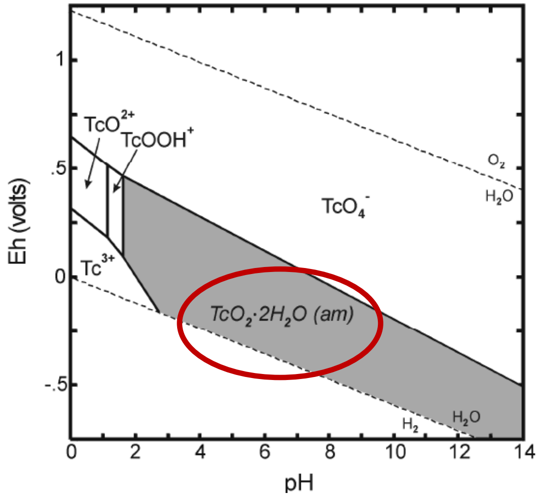
Remediation Research for Hanford

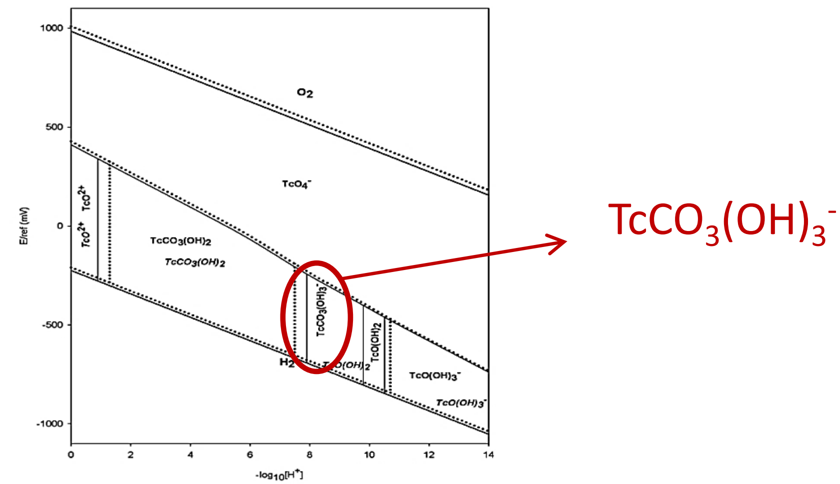
Investigate the fate of Tc under conditions relevant to the Hanford Site

FIU Applied Research Center

Objective

Study the partitioning of Tc-99 in the presence of bicarbonates under reducing conditions between the aqueous phase and Hanford soil





- Will Tc(VII) under reducing conditions, precipitate as TcO_2 or form soluble Tc(IV)- carbonate complexes under circumneutral conditions?

- And consequently, what is the fate of Tc(IV)-carbonate complexes? (e.g. sorption)

Remediation Research for Hanford

Investigate the fate of Tc under conditions relevant to the Hanford Site

FIU Applied Research Center

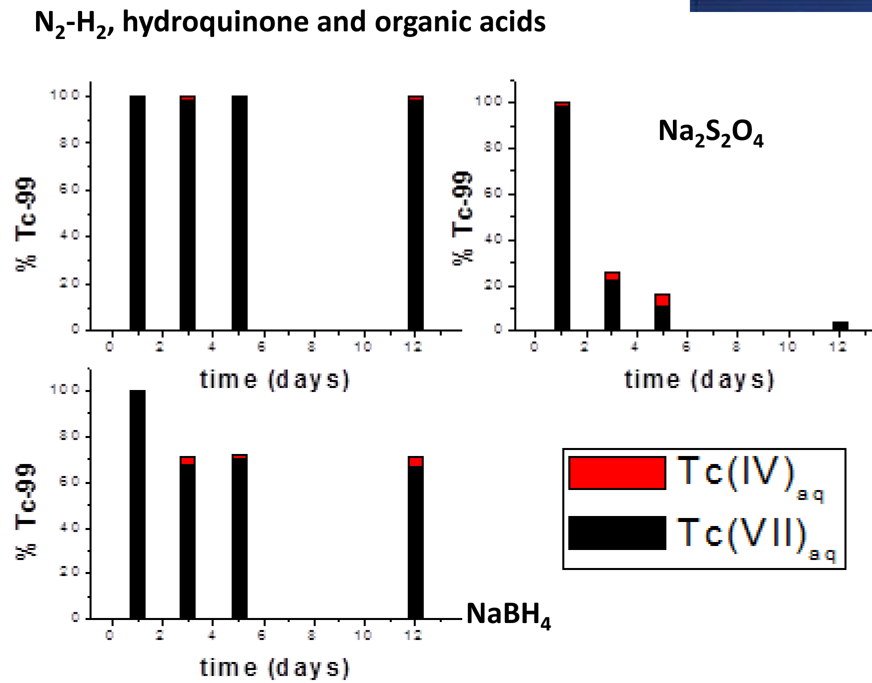
Experimental approach

Batch experiments containing Hanford soil were equlibrated in N_2-H_2 atmosphere with 50µM Tc-99, 10mM HCO_3^- in the presence of inorganic and organic reducing agents

Speciation of Tc in the aqueous phase was performed by organic solvent extraction (TPPC-CH_3Cl) which allows the determination of Tc(IV) and Tc(VII). Samples were analyzed by Liquid Scintillation Counting

Remediation Research for Hanford

Investigate the fate of Tc under conditions relevant to the Hanford Site



Highlights

- Preliminary results revealed complete reduction of Tc(VII) by $Na_2S_2O_4$ ($t_{1/2}$=6d).

- Reducing conditions induced by the presence of organic molecules (hydroquinone, formic and oxalic acid), did not impact Tc(VII) redox state. Electron donor distribution is more important than overall Eh values

- Partial reduction in the presence of 10^{-3}M $NaBH_4$, fast and complete reduction in the presence of $NaBH_4$ 10^{-2} and $SnCl_2$ 10^{-3}M

Remediation Research for Hanford

Investigate the fate of Tc under conditions relevant to the Hanford Site

Proposed Scope for FY 8

- Investigate the parameters that affect surface - mediated heterogeneous reduction of Tc(VII), such as the presence of electron donors, quantity and specific surface area.

Batch experiments using Hanford soil and pure minerals (magnetite and ilmenite) under reducing conditions in the presence of bicarbonates will be conducted.

- Study the bicarbonate range where mobilization of prior immobilized Tc by the soil may be facilitated under reducing conditions, due to Tc(IV) – HCO_3^- chemical affinity at circumneutral conditions.

Task 2 Remediation Research for Savannah River Site

Effect of acidification on soil properties at the SRS F/H Area acidic plume

Site needs

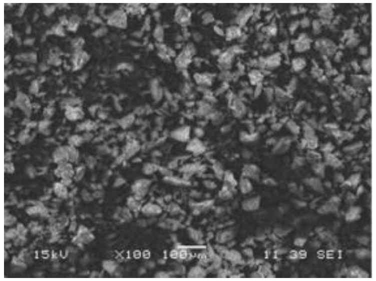
- Sediment's elemental composition and morphological properties are affected by the long term exposure to highly acidic conditions.
- Understand the chemistry of the acidic plume: effect of the soil acidification at F/H Area on its physico-chemical characteristics and its sorptive properties towards U(VI)

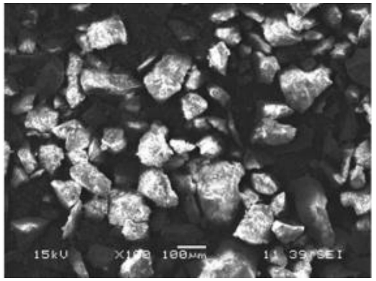
Remediation Research for Savannah River Site

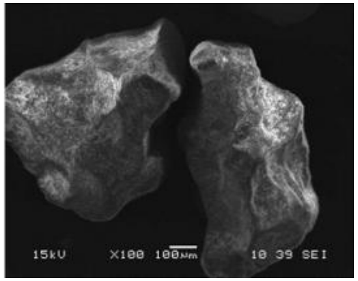
Effect of acidification on soil properties at the SRS F/H Area acidic plume

Objectives

- Investigate the change of the soil's morphological and physico-chemical characteristics (specific surface area, pore distribution) as a results of exposure to acid
- Correlate the changes in the soil's physico-chemical properties with its sorptive capacity towards U(VI)
- Compare the properties of the acidified soil with those of background soil from F/H Area







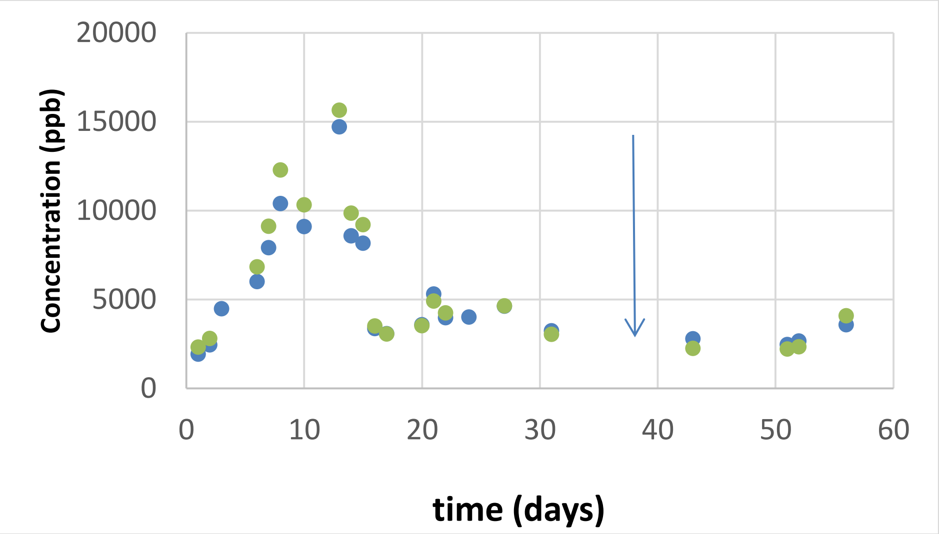
Remediation Research for Savannah River Site

Effect of acidification on soil properties at the SRS F/H Area acidic plume

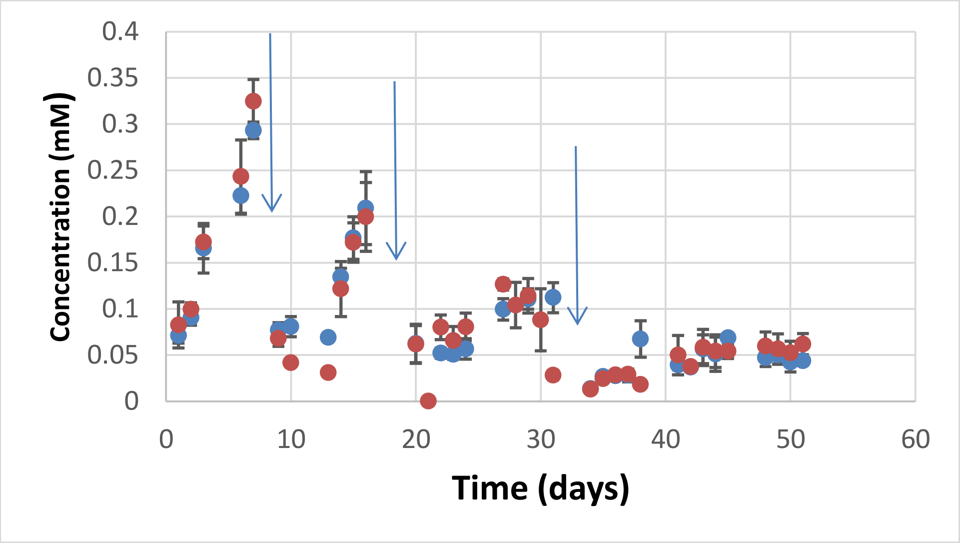
FIU Applied Research Center

Experimental approach

- Creation of acidified soil in the lab in batch experiments with occasional monitoring of Al, Fe and Si in the supernatant, due to kaolinite and goethite dissolution, with and without the formation of secondary precipitates (hematite and amorphous silica)



Al : green dots, Si: blue dots



Al: blue dots, Si: red dots

Remediation Research for Savannah River Site

Effect of acidification on soil properties at the SRS F/H Area acidic plume

Highlights

Prolonged exposure of soil to acid strips away the fine particle coating (kaolinite and goethite)

↓

Decrease of specific surface and Fe content

↓

Decrease of U(VI) sorption at both acidic and circumneutral conditions

- Plume soil exhibits higher Al and Si content compared to background soil, but the same Fe content and exhibits same U(VI) sorption at all pH values studied

Remediation Research for Savannah River Site

Effect of acidification on soil properties at the SRS F/H Area acidic plume

Concluding experiments

Kinetic experiments at circumneutral conditions using plume soil and background soil

Conference presentations

- STEM Research and Career Symposium, Emory University, Atlanta GA, October 1-3. DOE Fellow Ms. Awmna Rana recently got a travel award to present this research
- Waste Management 2018

Task 2 Remediation Research for Savannah River Site

Investigate interactions of Tc and I with soil from Four Mile Branch Wetland

New Task FY8

Site Needs:

I-129 is a major risk driver in the Fourmile Branch wetlands and SRNL work has shown that it binds strongly to organic-rich sediments. The wetlands are dynamic geochemically and as conditions change, I-129 is released.

Tc-99 is present in the Fourmile Branch wetlands and despite not being a major risk driver at SRS as it is in other DOE Sites, the Fourmile Branch wetlands is an excellent analogue for studying the behavior of Tc-99 in naturally organic-rich environments.

Objective

A better understanding of the chemistry of Tc-99 in the presence of NOM and of the bind/release mechanisms to control I-129 behavior in the wetlands and to account for seasonal releases during long-term monitoring.

Proposed approach

Batch experiments with Four Mile Branch Wetland soil and Tc and I under aerobic and anaerobic conditions

Batch experiments with commercially available humic acid and “model” organic polymers (e.g. poly-galacturonic acid or poly-styrenesulfonates or pyrogallol modelling carboxyl, sulfonate and phenol groups, respectively) will provide a better understanding of the Tc- and I- interactions with NOM

Task 2 - Application of Humic Acid for uranium remediation at SRS

Site Needs:

Huma-K has potential as amendment in treatment of uranium in groundwater associated with F-Area Seepage Basins plume. In addition, it is thought that elevated silica concentrations in the acidic plume may enhance uranium removal when pH is increased by base injection. Understanding the synergy between humate and silica is important to developing an optimized pH adjustment to treat uranium in groundwater.

Objectives:

- Investigate the synergy between colloidal silica and humic acid that may have an effect on the removal of uranium (U) from contaminated groundwater.
- Determine if the low cost unrefined humic acid (Huma-K) and modified humic acid (HA) can be used to control the mobility of uranium groundwater and study the sorption/desorption of humic acid (Huma-K) and modified HA on SRS sediment at various pH via batch and column experiments
  - Perform batch and column sorption experiments with humic acid to simulate the creation of a sorbed humate treatment zone in acidic groundwater contaminated with U

Task 2 - Application of Humic Acid for uranium remediation at SRS

Accomplishments Year 7:

The Synergistic Effect of Humic Acid and Colloidal Silica

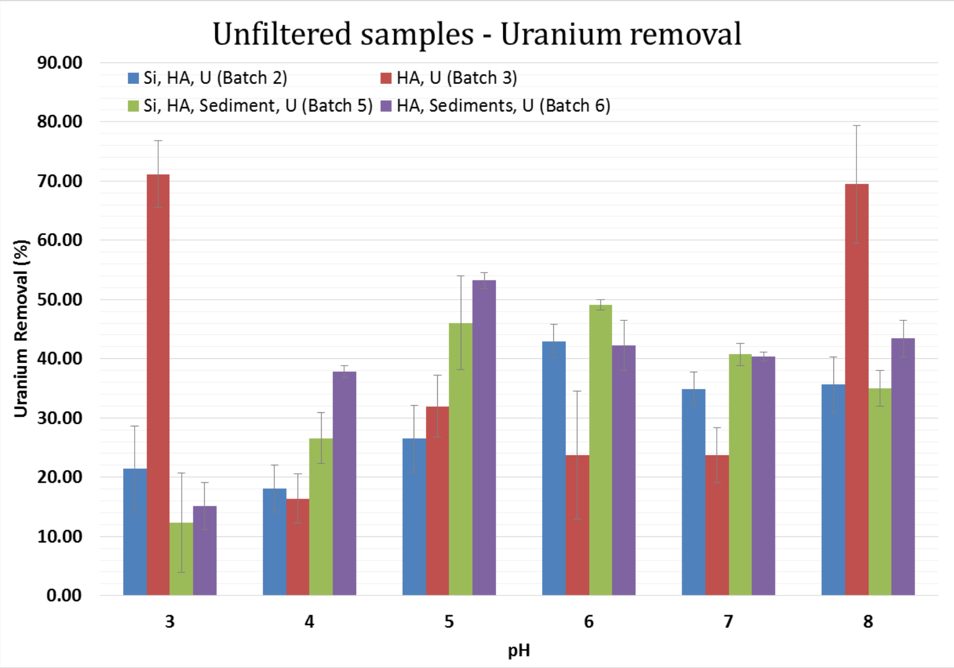
- Studied synergetic interactions between humic acid and colloidal silica on uranium (U) removal at 30 ppm U and varying pH.

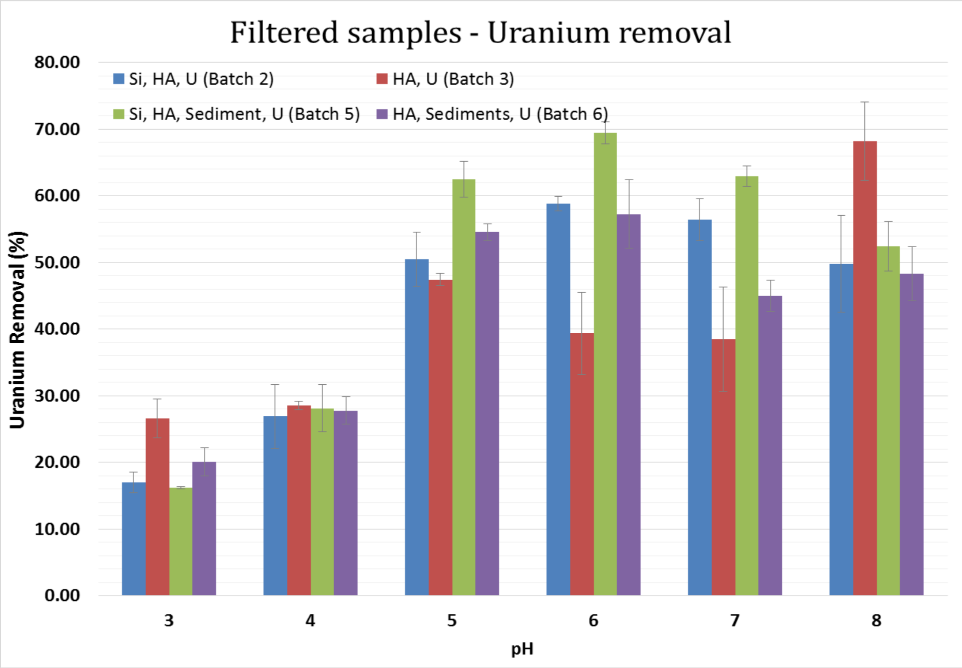
- Prepared batch samples with combinations of HA, Si, U and sediment with a pH 3 - 8. Prepared samples for analysis of U(VI) by KPA.
  - Batch 2: Si (3.5 mM) + U(VI) (30 ppm) + HA (50 ppm), (no sediments)
  - Batch 3: U(VI) (30 ppm) + HA (50 ppm), (no Si or sediments)
  - Batch 5: Sediments + Si (3.5 mM) +U (VI) (30 ppm) + HA (50 ppm)
  - Batch 6: Sediments + U(VI) (30 ppm) + HA (50 ppm), (no Si)
  - Control: U(VI) (30 ppm), (no SI, HA, or sediment)

- Analyzed filtered and unfiltered samples to estimate uranium removal for aqueous phase

The Synergistic Effect of Humic Acid and Colloidal Silica

- Uranium removal increased with increase in pH to pH 5 and remained constant with increase in pH. This is true for both filtered and unfiltered samples.
- At 0.5 ppm U(VI), batches containing sediment showed higher removal compared to sediment-free samples.
- At 30 ppm U(VI), similar uranium removal was observed for both sediment and sediment-free samples.
  - It is hypothesized that sorption sites on the sediment are saturated and additional uranium binds with humic acid and Si resulting in similar removal among all the batches.



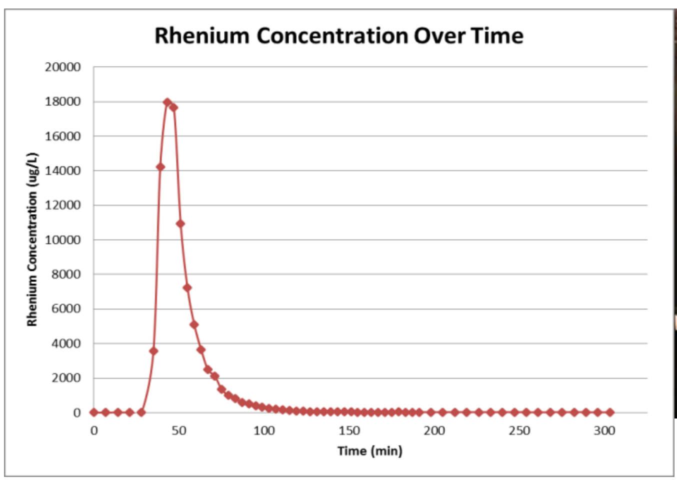


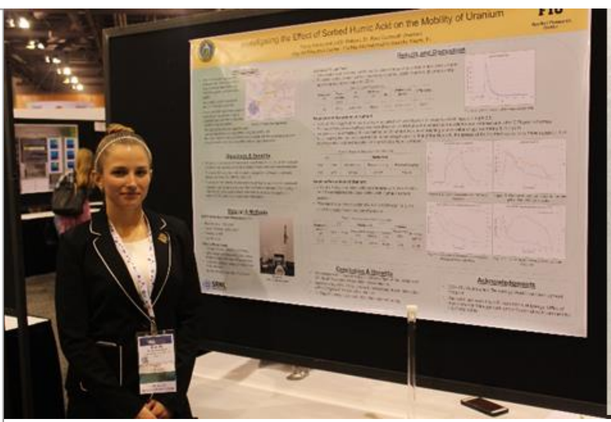
Task 2 - Application of Humic Acid for Uranium Remediation at SRS

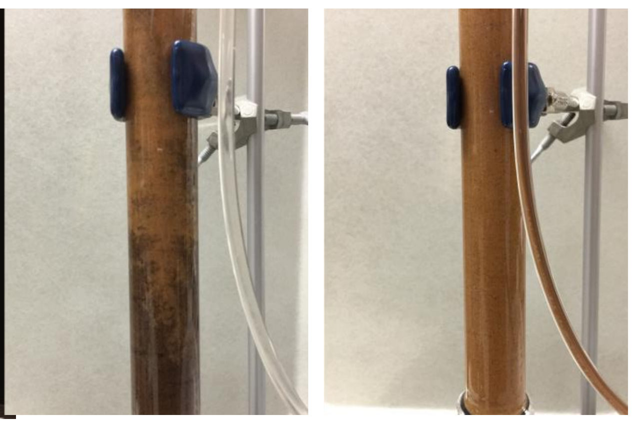
FIU Applied Research Center

Humic acid batch and column experiments

- Performed a rhenium tracer test 2.93 mL of 250 ppm rhenium solution (0.7325 mg), samples were collected over a time, data analysis concluded that 0.75 mg of rhenium was recovered from the column at 102% recovery with an effective flow rate of 1.97 mL/min.
- A column was conditioned with artificial ground water (AGW) adjusted to pH 3.5 to mimic the SRS water conditions. After reaching a steady pH of 3.46, approximately 80 ml of 10,000 ppm modified humic acid was injected into the column followed by AGW at pH 3.5.
- After the concertation of humic reached around 2% of initial concentration, 2 PV of 100 ppb uranium solution was injected into the column followed by 2 PV of AGW at pH 3.5, 4.5, and 5.5 (Analysis are in progress).







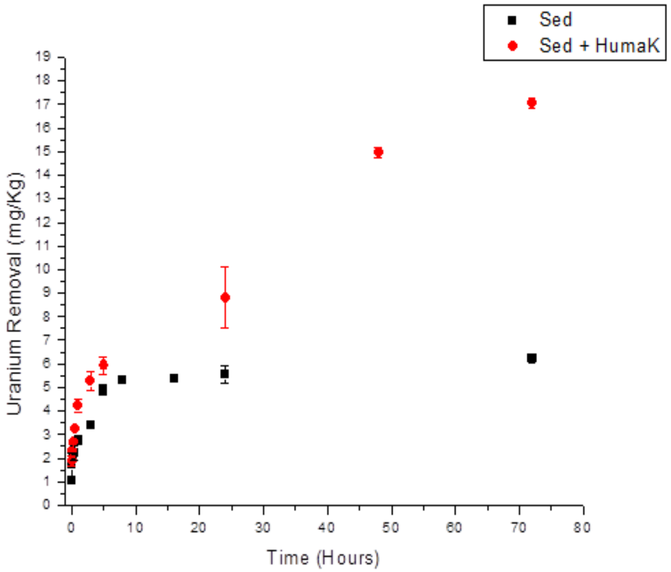
Humic acid column experiment

Task 2 - Application of Humic Acid for uranium remediation at SRS

Accomplishments Year 7:

Batch Experiments with Humate

- Conducted batch sorption experiments to study the effect of ionic strength in Huma-K sorption.
  - Huma-K sorption increases with the increase of ionic strength at pH 4-7.
- Conducted potentiometric titrations of Huma-K, humic acid, and modified humic acid.
- Conducted kinetics experiments of uranium sorption onto SRS sediments with and without Huma-k coating at pH 4.
  - Presence of Huma-K in sediments increases uranium removal; but, it takes longer time to reach equilibrium compared to plain sediment
- A manuscript on the sorption properties of Huma-K injected into the groundwater is under peer review in the *Chemosphere*.



Kinetics of U(VI) sorption onto SRS sediment

Task 2 – Remediation Research and Technical Support for Savannah River Site

Proposed Scope for Year 8

Site Needs:

Huma-K can effectively treat uranium in groundwater at acidic conditions. Yet, it is equally important to know the maximum pH at which Huma-K still provides beneficial treatment of uranium. For SRS needs, this is important because if Huma-K or other humic amendments are to be used as a supplement or replacement for base injection, then the amendments will have to provide some benefit at pH values near 5. Furthermore, uranium plumes at other sites are often at pH values exceeding 5 and this task will help to define the conditions for which humic amendments are applicable.

Objectives:

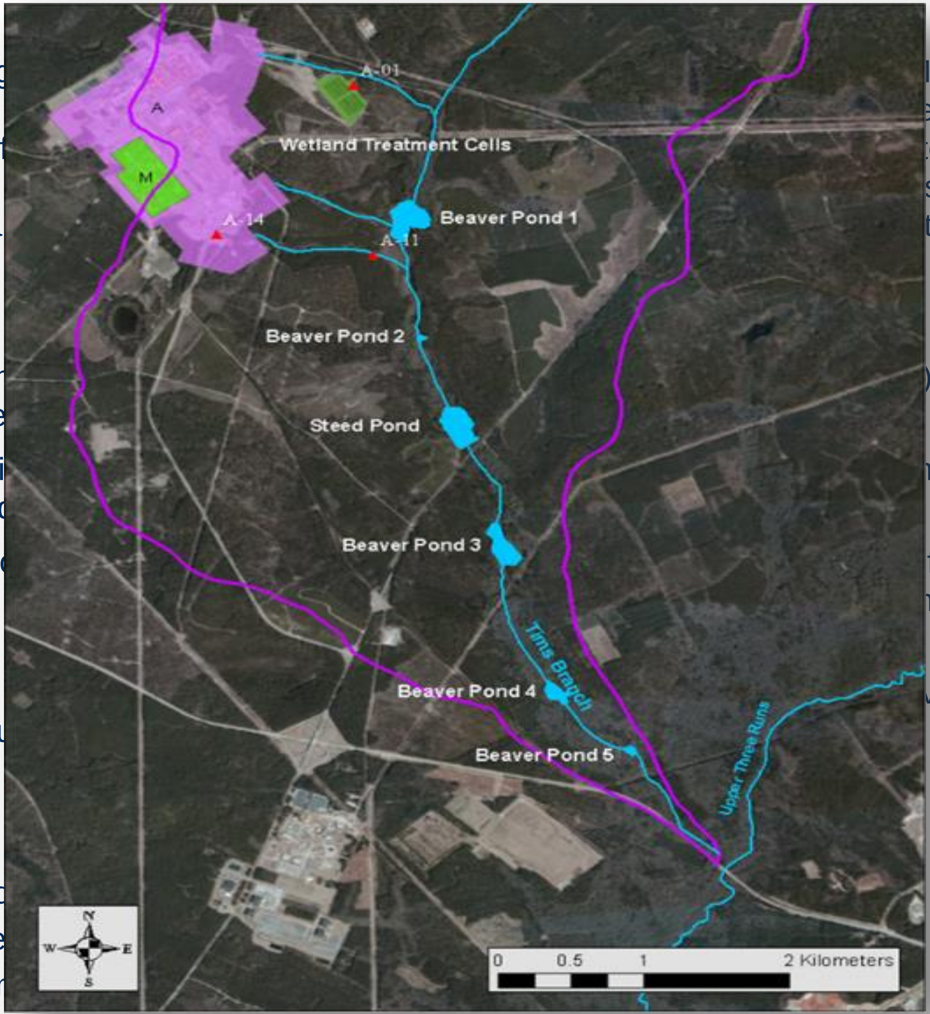
- Explore the effect and mechanisms of synergetic interactions between HA and colloidal silica that controls uranium behavior in a range of environmental variables such as pH and soil minerals.
- Evaluate the effect of time, pH, and initial uranium concentrations on U(VI) sorption/ desorption behavior using experimental matrix that includes SRS sediment, U(VI), Huma-K or modified humic substances.
- Study the effect of competitive sorption of uranium with different metals (Ag^{+}, Zn^{2+}, and Ce^{3+}) onto SRS sediment amended with Huma-K.
- Study the long term performance behavior of HA under varied pH levels via column experiments; the results from the laboratory studies can then be correlated with the injection tests previously conducted in the field.

Task 3 – Surface Water Modeling of Tims Branch

FIU Applied Research Center

Site Needs:

According to DOE EM’s Technolog l Innovation and Technology Program, a number of issues still e contamination at SRS and other DOE EM sites. Utilization of ool to evaluate hydrological impacts on the fate and transport s) will be beneficial to SRS, particularly if the tool developed ca tes.



Objectives:

- Develop a physically based num) of Tims Branch using open source and commercial software
- Develop a transport model to si ns Branch and support long-term monitoring of tin (Sn)-based
- Develop a transferable technol fate and transport of major contaminants of concern (e.g. her Hg-contaminated stream systems at SRS and other DOE
- Collect *in-situ* field data such velocity, suspended particle concentration and other water qu

Present (Year 7) Subtasks:

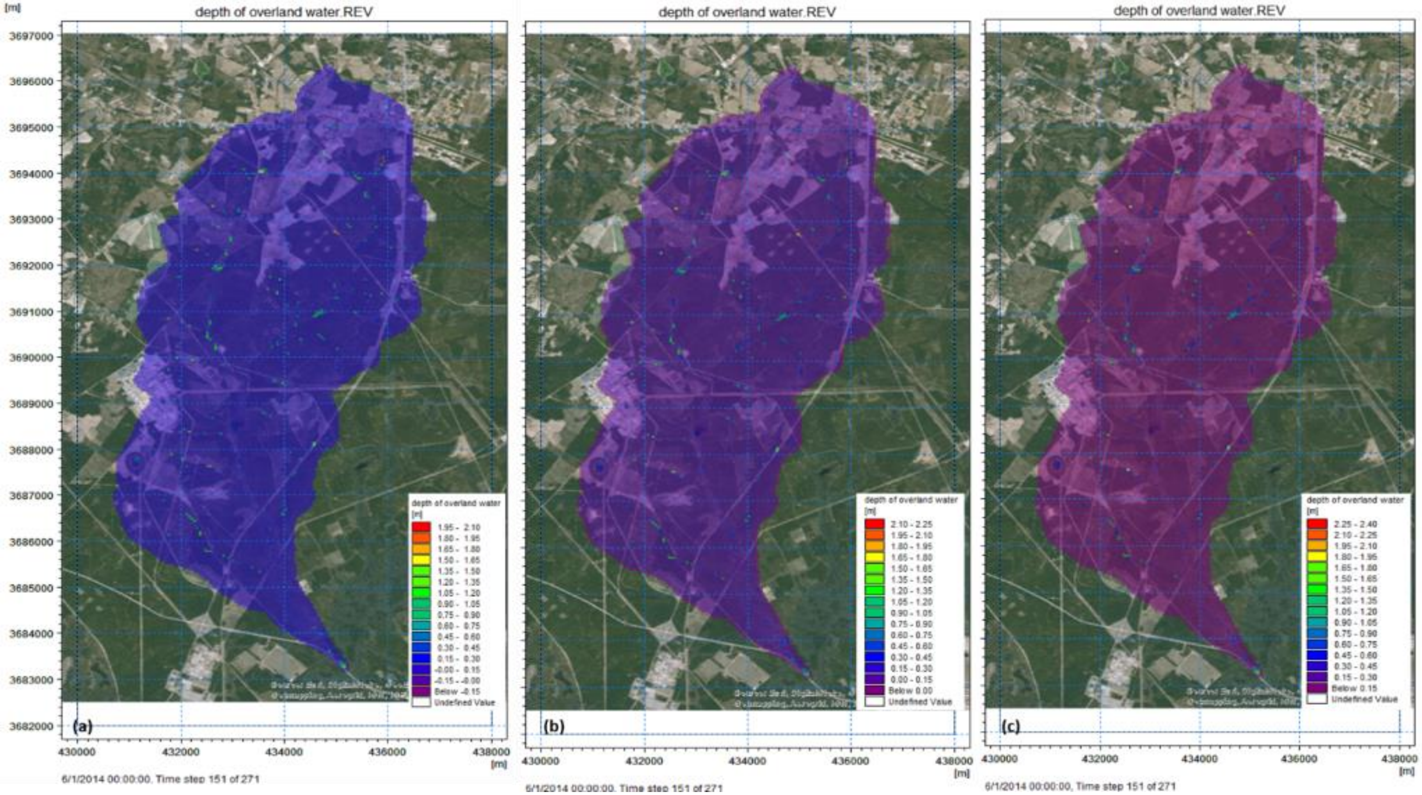
- Modeling of Surface Water and
- Application of GIS Technologie
- Biota, Biofilm, Water and Sedi

Task 3 – Surface Water Modeling of Tims Branch

Accomplishments Year 7:

2-D Overland Flow (OL) Model

- Developed 2-D OL flow model using MIKE SHE.
- Model calibration and sensitivity analyses in progress.



Task 3 – Surface Water Modeling of Tims Branch

FIU Applied Research Center

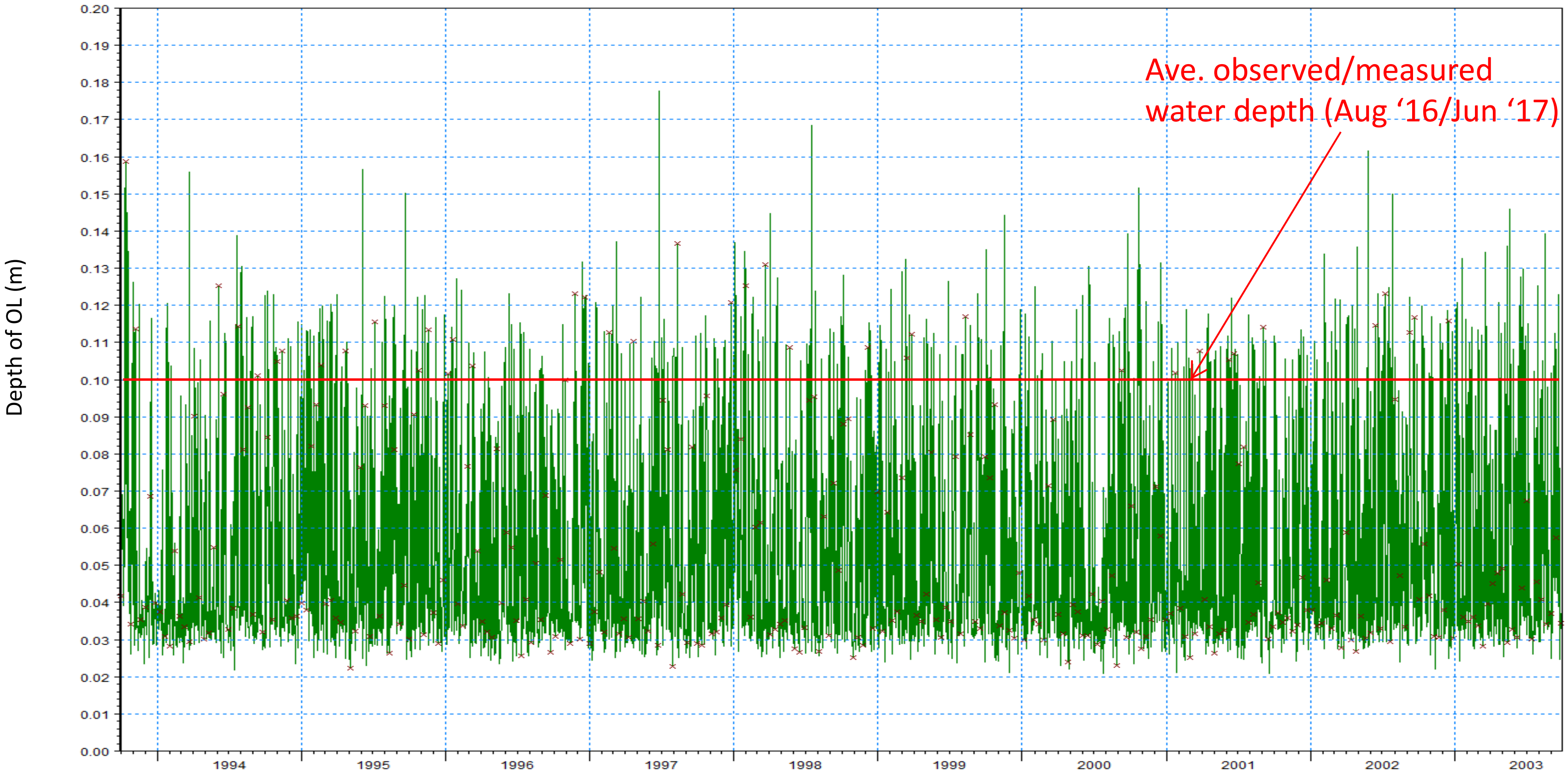
Parameter	Value	Number of Simulations	Total Simulation Time (hrs)	Results
Detention Storage (mm)	0.0, 2.5 (± 5%, ±10%, ±15%, ±20%)	10	80	Insensitive
Surface-Subsurface Leakage (sec^{-1})	0.0, 0.0001 (± 5%, ±10%, ±15%, ±20%)	10	80	Insensitive
Initial Water Depth (m)	From previous simulation	22	176	Highly Sensitive
Separated Flow Area	Yes/No	2	16	Highly Sensitive

Each simulation approximately took 8.00 hours to complete. Some of the simulations were repeated due to numerical errors that were encountered. The simulations will be repeated after coupling with stream flow model (MIKE 11).

Task 3 – Surface Water Modeling of Tims Branch

Graph depicts 10 yrs simulated overland flow depth at confluence of Tims Branch (TB) and Upper Three Runs.

Average measured (observed) data collected in TB in August 2016 and June 2017 correlate well with the average simulated results.

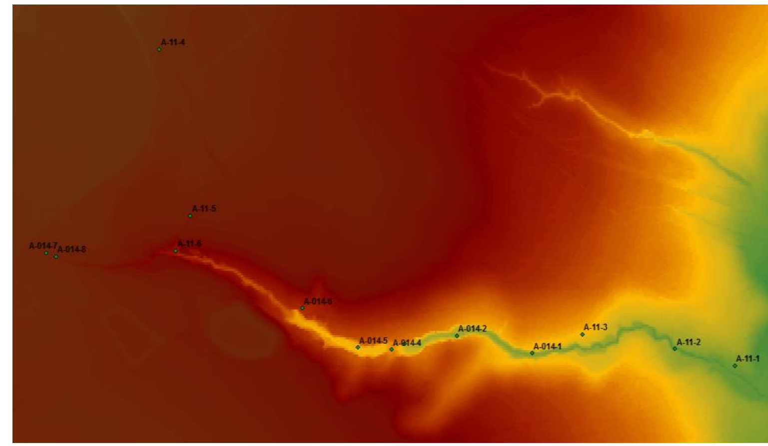


Task 3 – Surface Water Modeling of Tims Branch

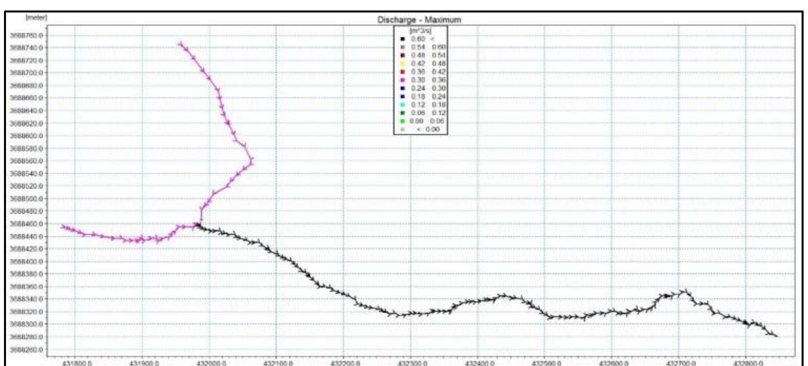
Accomplishments Year 7:

1-D Stream Flow (SF) Model

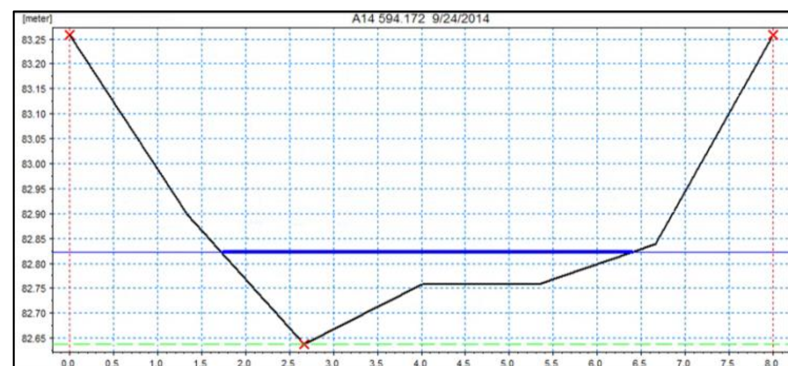
- Developed 1-D SF model of A-014 outfall tributary using MIKE 11.
- Field data collected in August 2016 (Year 6) implemented in model.
- Model calibration and sensitivity analyses in progress.



Sample locations along A-014 OF tributary where cross-section profiles were measured.



Field cross section data implemented in MIKE 11 for simulation of stream flow.



Cross section profile as viewed in MIKE 11.

Task 3 – Surface Water Modeling of Tims Branch

<u>Accomplishments Year 7</u>:

In-Situ Data Collection at Tims Branch

- Field sampling & *in-situ* data collection incorporated into DOE Fellow summer internship at SREL (in collaboration with SRNL).
- Follow-up field work conducted in June 2017, coordinated with student internship.
- Data supports model development & calibration.

In-Situ Data Collection at Tims Branch, SRS

Task 3 – Surface Water Modeling of Tims Branch

Proposed Scope for Year 8

Objectives:

- Model Calibration (completion of MIKE SHE OL flow and MIKE 11 SF models sensitivity and uncertainty analyses) .
- Coupling of stream flow and overland flow models.
- Data analysis & visualization using GIS and statistical tools.
- Field sampling, *in-situ* and remote data collection.
- Begin preliminary development of 1-D stream flow (SF) model of main Tims Branch stream using MIKE 11 (field data and measurements collected in July 2017 to be implemented).
- Preliminary development of solute transport model.

Task 5: WIPP Collaboration

Objective: To update experimental sorption data for Actinides for the WIPP Performance Assessment 5-year re-certification

Initiate Collaboration

- LANL postdoc (Tim Dittrich) and ARC postdoc (Hilary Emerson)
- Fall 2015

Deploy FIU-ARC postdoc

- 8 weeks as a visiting scientist
- Learn to conduct mini column experiments
- February – April 2016

Conduct parallel experiments

- Parallel experiments with more basic science focus at FIU
- 2016-2017

Long-term partnership

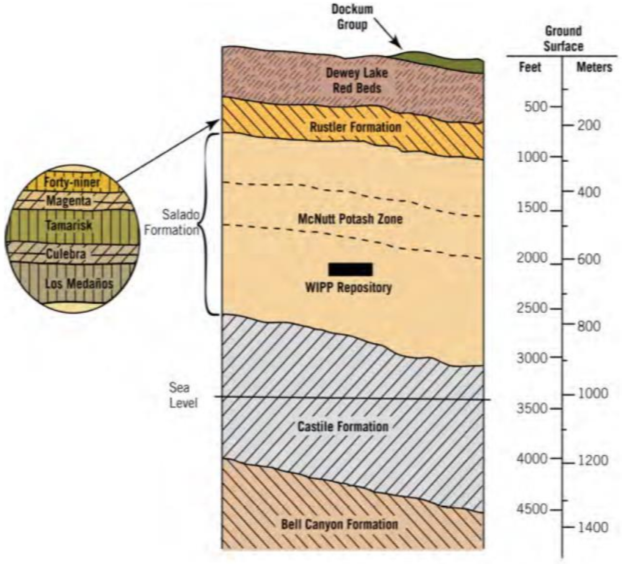
- Continue WIPP-related research as part of the DOE-EM cooperative agreement
- 2017 and beyond!

Accomplishments Work presented at AGU 2016, McNair 2016, LSSF 2017, Waste Management 2017, and ABC Salt V 2017 Workshop hosted by LANL

Task 5: WIPP Collaboration

Site Needs:

There is a lack of relevant experimental sorption data for trivalent actinide and lanthanide interactions with Culebra dolomite. These data are important for the WIPP performance assessment (PA). The previous PA assumed a K_d of 20-400 mL/g for Pu and Am. However, sorption K_d values have been measured from $10^{3.4}$ to 10^6 mL/g (e.g. Brady *et al*., 1999; Perkins *et al*., 1999; Brush & Storz, 1996). Therefore, there is a need to decrease the uncertainty in these parameters.



Year 7 Objectives:

To update experimental sorption data for actinides under simplified systems to complement LANL ACRSP research for the WIPP 5-year re-certification:

- Evaluate trivalent actinide and lanthanide sorption parameters for dolomite at variable ionic strength.
- Investigate the sorption capacity of dolomite minerals for trivalent actinides and lanthanides.

Present (Year 7) Tasks:

1. Conduct mini column saturation experiments for Nd at 0.1 and 5.0 M NaCl.
2. Analyze equilibrium and kinetic sorption parameters for Nd at variable ionic strength (0.01 to 5.0 M) in batch experiments.
3. Characterize solid phases following interaction with variable ionic strength brines and Nd.

Oxidation State Distribution of Key Actinides in WIPP Performance Assessment

Actinide	Oxidation State				Speciation Data used in Model Predictions
	III	IV	V	VI	
Uranium		50%		50%	Thorium for U(IV), 1 mM fixed value for U(VI)
Plutonium	50%	50%			Am/Nd for Pu(III) and thorium for Pu(IV)
Americium	100%				Americium/neodymium

Task 5: WIPP Collaboration

Applied Research Center

Research Highlights

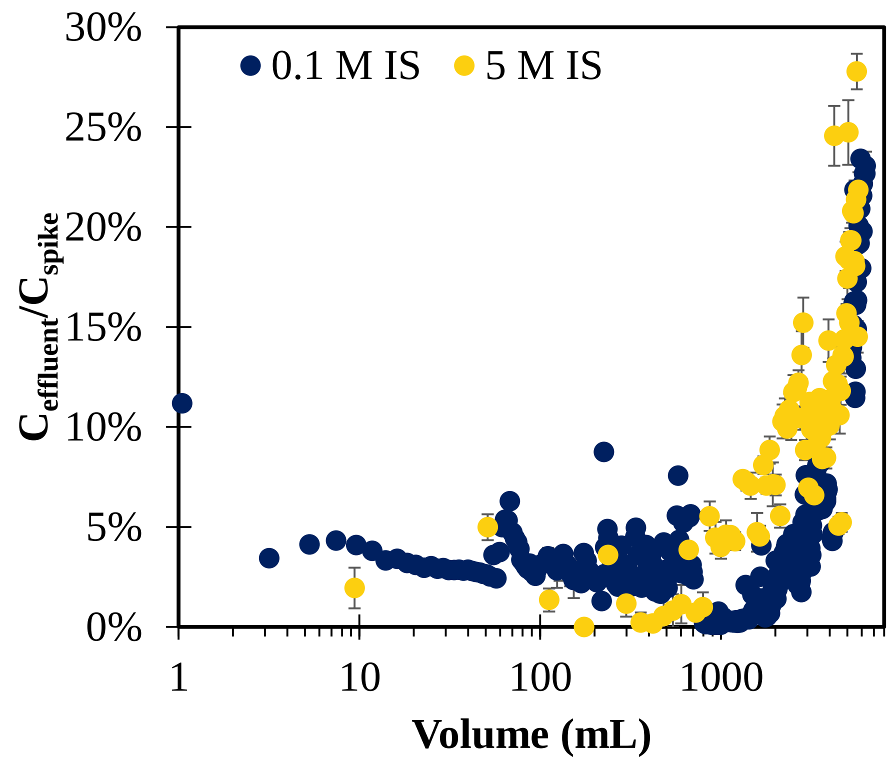
Established relationship with LANL-CEMRC

- Feb-Apr 2016 deploy ARC postdoc to LANL CEMRC
- Jun-Aug 2017 deploy DOE Fellow & ARC postdoc

Results highlight conservatism in WIPP PA sorption assumptions

- Conducted batch and mini-column experiments to investigate Nd(III) sorption as an analog to Am/Pu(III)
- Showed that the fundamental mechanisms controlling removal of Nd change depending on flow (i.e. sorption versus incorporation processes)

IS	pC_{H+}	K_d (mL/g)
5.0 M	8.28±0.38	6380±3060
2.0 M	8.22±0.43	1180±450
1.0 M	8.41±0.38	819±225
0.1 M	8.59±0.38	724±105
0.01 M	8.60±0.39	503±129



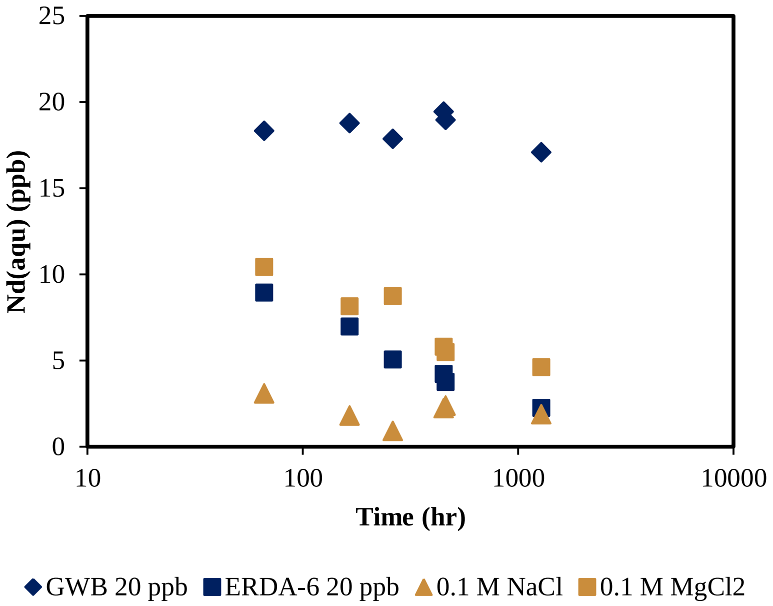
WIPP PA assumes K_d of 20-400 mL/g

Task 5: WIPP Collaboration

Accomplishments Year 7:

- Established a relationship with LANL ACRSP
  - Feb-Apr 2016 deployed ARC postdoc to LANL ACRSP
  - Jun-Aug 2017 deploy DOE Fellow & ARC postdoc to LANL ACRSP (Summer Internship)
- Conducted batch and mini-column experiments to investigate Nd(III) sorption as an analog for Am/Pu(III)
- Presented work at AGU 2016, McNair 2016, LSSF 2017, Waste Management 2017, ABC Salt V 2017 with upcoming presentations at LANL Summer Intern symposium and ACS Fall 2017 (accepted)
- Progress Report submitted May 2017

Crosscutting research bridges the basic and applied sciences



Experiments with WIPP synthetic brines (blue, LANL) versus simplified salt systems (yellow, FIU) help to understand which parameters control the system.

FIU Applied Research Center

Task 5: WIPP Collaboration

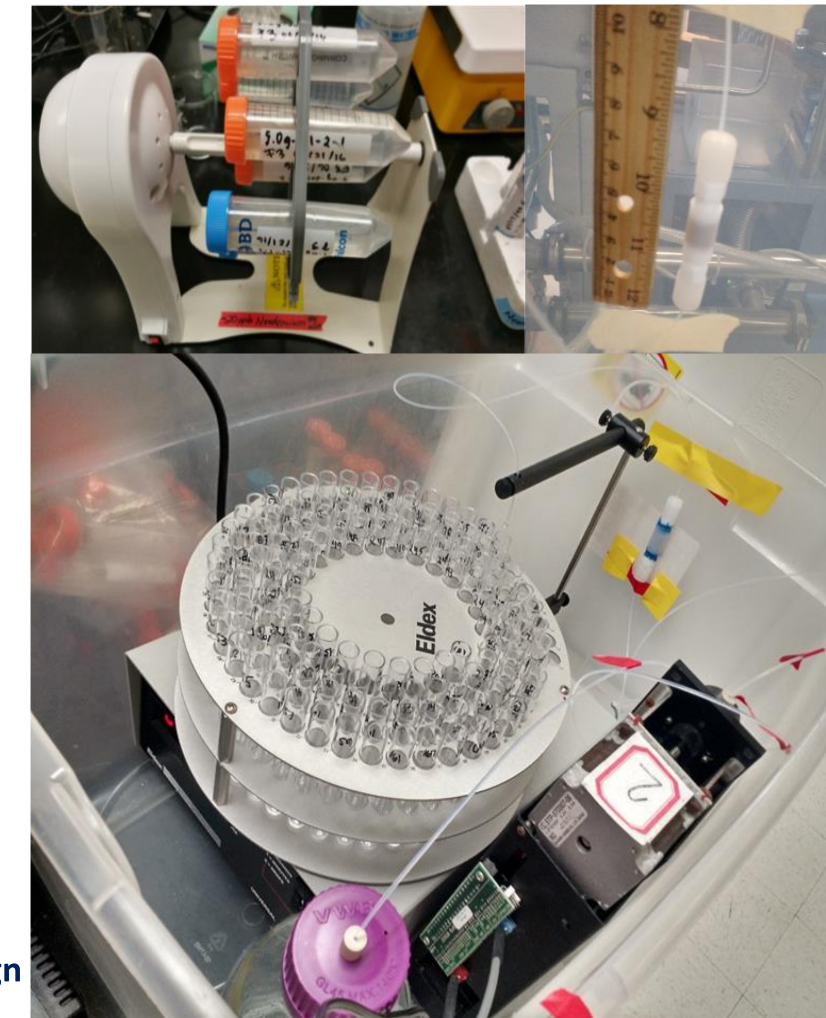
Proposed Scope for Year 8

Site Needs:

The effects of ligands in the waste stream (e.g. EDTA and oxalate) on near field mobility of actinides is still unknown (Dunagan, 2007; Brush, 1990). Complexation constants have been measured for most actinides and lanthanides (Thakur *et al*., 2014; 2015; Borkowski *et al*., 2001). However, their long-term stability and sorption are not yet understood.

Objectives:

1. Develop capabilities for analysis of EDTA (and complexes) in the aqueous phase.
2. Measure sorption parameters for Nd/Am(III), Th(IV), and U(VI) complexed with EDTA at variable ionic strength.
3. Compare mobility of Nd (Year 7 results) versus Nd-EDTA.



Mini column experimental design based on Dittrich (2015) report